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Electronic transitions in *cis*- and *trans*-dichloroethylenes and tetrachloroethylene

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Electronic structures of *trans*- and *cis*-dichloroethylenes and tetrachloroethylene were studied using symmetry-adapted cluster configuration interaction theory. Basis sets up to the aug-cc-pVTZ of Dunning, Jr., augmented with appropriate Rydberg functions were used for the calculations. The results derived in the present study show good agreement with the available experimental values. In all cases, the main bright excitation was the $\pi \rightarrow \pi^*$ transition. The other vertical excitations, $\pi \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, and $n \rightarrow \pi^*$, which have not been studied before, were also investigated. First Rydberg series involving transitions from the π orbitals to one 3s, three 3p, and five 3d orbitals were identified clearly. Several new assignments and reassignments of features in the experimental spectra were suggested. Contrary to earlier prediction, two $n\text{-}\sigma^*$ states, along with a $\pi\text{-}\sigma^*$ state in the dichloroethylenes, were calculated to be located above the main $\pi\text{-}\pi^*$ state. Accordingly, crossing between both the $n\text{-}\sigma^*$ states with the bright $\pi\text{-}\pi^*$ state is highly likely, unlike conclusions made in the earlier studies. This indicates that the photodissociation mechanism proposed by the earlier calculations warrants revision. Several low-lying triplet excited states were also studied. Electronic spectra of *trans*-1-chloro-2-fluoroethylene and *cis*-1-chloro-2-fluoroethylene were also calculated. The $\pi \rightarrow \pi^*$ transitions of these haloethylenes are compared and interpreted in terms of the inductive and resonance effects. © 2008 American Institute of Physics. [DOI: 10.1063/1.3002911]

I. INTRODUCTION

Chloroethylenes are atmospheric pollutants that have many adverse effects on humans, including cancer. Thus, it is important to know the spectroscopic properties and the photochemistry of these pollutants. The vacuum ultraviolet absorption spectra of ethylene and its halogen derivatives have long been of interest, since a variety of excitations have been observed. There have been many experimental studies aimed at understanding the electronic structures of chloroethylenes.^{1–20} Robin^{21,22} reviewed the electronic spectra of haloethylenes, including chloroethylenes, but a clear picture about the electronic transitions in the chloroethylenes is yet to emerge not only because the assignments and properties of the electronic states involved in the transitions are ambiguous but because even some of the fundamental transitions have not been found yet. For example, the Rydberg $\pi \rightarrow 3s$ transition was seen only in vinyl chloride and in tetrachloroethylene, although this $\pi \rightarrow 3s$ transition is allowed in all the chloroethylenes because of the nature of their symmetries. One reason that this transition was not observed might be that since the main peak, i.e., $\pi \rightarrow \pi^*$ band, in the

experimental spectra is broad for chloroethylenes, these $\pi \rightarrow 3s$ transitions are probably superimposed by the $\pi\text{-}\pi^*$ bands.¹⁴

Some inconsistent and speculative assignments were made in past studies. For example, a study by Walsh² claimed that the origin of the $\pi \rightarrow 3s$ band in the spectrum of tetrachloroethylene was below 6.20 eV, whereas Goto⁵ showed the $\pi \rightarrow 3s$ band beginning at 6.58 eV. Robin²¹ tentatively concluded that the band in Walsh's² spectrum might be an impurity band and assumed that Goto's⁵ result was correct, pending confirmation of the spectrum. So, the $\pi \rightarrow 3s$ transition in tetrachloroethylene is ill defined. The $n\text{-}\sigma^*$ states through which chloroethylenes are supposed to dissociate were not identified for many chloroethylenes. In several spectra of chloroethylenes, there is an unexpected band on the low-frequency wing of the $\pi \rightarrow \pi^*$ excitation, most easily seen at 6.01 eV in *trans*-dichloroethylene and at 5.39 eV in tetrachloroethylene. These bands were roughly assigned to $\pi\text{-}\sigma^*$ bands.²² A recent report²³ based on the experimental study on dichloroethylenes loosely referred to the $\pi \rightarrow \pi^*$ band as the $\pi \rightarrow \pi^*$ state due to lack of clear evidence for individual transitions in the absorption spectra, although there is more than one transition under this band. Likewise, the next higher energy band was referred to as the $n\text{-}\sigma^*$ state, although it contains two singlet and two triplet states.²³ In a nutshell, it is apparent that the assignments and properties of

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the electronic states involved in the transitions in chloroethylenes are not clear.

The photodissociation of chloroethylenes has received much attention in the field of photochemistry for obvious reasons.^{20,24–34} Possible photochemical activities include isomerization, Cl atom detachment, HCl elimination, and molecular Cl₂ elimination. Although the photochemistry of the chloroethylenes in the wavelength region around 200 nm has been extensively studied through experiments, the details of the reaction mechanisms are still poorly understood [that is, except for vinyl chloride, for which a clear picture is established regarding its photodissociation. There are two main dissociation pathways: one is the transition to the dissociative $n\text{-}\sigma^*$ state from the initially excited $\pi\text{-}\pi^*$ state resulting from level crossing, which gives higher energy Cl fragments, and the other is the internal conversion to the $\pi\text{-}\sigma^*$ state or ground state (see Ref. 35 and the citations therein).]. This is because in this energy region a variety of electronic transitions, including the valence and Rydberg transitions, exist. Through a few low-level calculations, some approximate conclusions were made in the past regarding the dissociation mechanisms in chloroethylenes, especially on Cl atom detachment. The most referred photodissociation study on chloroethylenes is the photofragment translational study by Umemoto *et al.*²⁷ Their experimental results showed that there are two Cl detachment channels in dichloroethylenes and, according to their simple *ab initio* calculations with the 4-31 G basis set, dichloroethylenes possess two $n\text{-}\sigma^*$ states near the $\pi\text{-}\pi^*$ state.²⁷ The second $n\text{-}\sigma^*$ state, similar in nature to the $n\text{-}\sigma^*$ state of vinyl chloride, is located above the $\pi\text{-}\pi^*$ state. Accordingly, this dissociative $n\text{-}\sigma^*$ state crosses the bright $\pi\text{-}\pi^*$ state, which leads to fast C–Cl bond dissociation. Since the first $n\text{-}\sigma^*$ state is always well below the $\pi\text{-}\pi^*$ state,²⁷ potential crossing between these two states is not expected. Therefore, according to their calculations, predissociation from the $\pi\text{-}\pi^*$ state to the first $n\text{-}\sigma^*$ state is not likely to occur. It should be noticed here, on the other hand, that the calculated transitions by Kato *et al.*,³⁶ in order of increasing energy, are $\pi\text{-}\sigma^*$, $\pi\text{-}\pi^*$, $n\text{-}\sigma^*$.

The second Cl detachment channel in the dichloroethylenes has been explained in the following way. In *trans*-dichloroethylene, the second $\pi\text{-}\sigma^*$ state, according to the calculations by Umemoto *et al.*,²⁷ is located below the lower $n\text{-}\sigma^*$ state. It has been proposed that the vibrationally excited levels of the $\pi\text{-}\sigma^*$ state may play the role of intermediate states for the transition to the first $n\text{-}\sigma^*$ state. Their assumption was that the $\pi\text{-}\sigma^*$ state is a bound state. Thus, the low-energy Cl fragments observed in their study are considered to originate from this first $n\text{-}\sigma^*$ state. All of these tentative conclusions were drawn from the results obtained in their calculations using the 4-31 G basis set. Mo *et al.*²⁹ also proposed dissociation mechanisms in chloroethylenes based on the results obtained by Umemoto *et al.*²⁷ by considering that the first $n\text{-}\sigma^*$ state is located below the main $\pi\text{-}\pi^*$ state and the first excited state S_1 ($\pi\text{-}\sigma^*$ or other) is a bound state. However, it is obvious that the reliability of the results obtained in these low-level calculations can be in doubt. If the situation was different, i.e., if the locations of these excited states were different, then the whole mechanism proposed

for the photodissociation of the chloroethylenes could become void. Note that it has already been proved using high-level *ab initio* calculations^{35,37,38} that the $\pi\text{-}\sigma^*$ state of vinyl chloride is a repulsive state, contrary to the conclusions made by Umemoto *et al.*²⁷ Note also that the singlet $n\text{-}\pi^*$ states may also have a role in the photochemistry of chloroethylenes; however, the location of these states has not been identified completely, so it is necessary to know the accurate electronic structure of these chloroethylenes to understand their photodissociation mechanisms.

It is important to know not only the singlet states but also the triplet excitations in the chloroethylenes since a few earlier studies supported that chloroethylenes, especially dichloroethylenes, dissociate through their triplet states.^{24,26,28} No high-level theoretical studies were made in the past on chloroethylenes except the studies on vinyl chloride.

The foregoing facts necessitated the present high-level electronic structure calculations on chloroethylenes. In continuation of our previous studies on haloethylenes,^{35,39} in the present investigation we studied the electronic spectra of *trans*- and *cis*-dichloroethylenes and tetrachloroethylene using the symmetry-adapted cluster⁴⁰/configuration interaction^{41–43} (SAC-CI) theory. The purpose of the present study was to obtain the electronic spectra of these two dichloroethylenes and tetrachloroethylene and to assign their valence as well as their Rydberg transitions, and this includes both singlet and triplet excitations.

II. COMPUTATIONAL DETAILS

All computations were performed with the GAUSSIAN03 suite of programs.⁴⁴ The vertical absorption spectra were obtained using the SAC-CI singles and doubles (SD)-*R* method with LevelThree accuracy utilizing the valence triple-zeta basis set of Dunning, Jr. without *d* polarization function for H atoms, hereafter cc-pVTZ(–*d*), and the augmented valence triple-zeta basis sets, aug-cc-pVTZ, of Dunning, Jr. for all other atoms.⁴⁵ These basis sets were duly augmented with two sets of Rydberg *spd* functions for carbon ($\zeta_s=0.0437$ and 0.017 25, $\zeta_p=0.0399$ and 0.015 75, and $\zeta_d=0.0285$ and 0.011 25), two sets for chlorine ($\zeta_s=0.0475$ and 0.018 75, $\zeta_p=0.0380$ and 0.0150, and $\zeta_d=0.0285$ and 0.011 25), and two sets for fluorine ($\zeta_s=0.0684$ and 0.0270, $\zeta_p=0.0551$ and 0.021 75, and $\zeta_d=0.0285$ and 0.011 25). This basis set combination provided accurate results on previous occasions.^{35,39} In all of the cases, the electronic spectra include possible singlet valence excitations, as well as the first Rydberg series involving transitions from the highest occupied molecular orbital, obviously π orbitals in the present case, to Rydberg 3*s* (one), 3*p* (three), and 3*d* (five) orbitals. Several low-lying triplet excitations were also studied. For convenience, throughout the paper we use “ σ ” and “ π ” to denote in-plane and out-of-plane Rydberg orbitals (*np* and *nd*), respectively, whereas π^* refers to C=C π^* orbitals and σ^* belongs to the C–Cl bond. Vertical excitation energies for all the selected haloethylenes were obtained at their respective experimental geometries taken from the literature.

TABLE I. Low-lying singlet excited states of *trans*-dichloroethylene obtained using SAC-CI at experimental geometry (Ref. 47) [excitation energies (ΔE), oscillator strengths (f), and second moments ($\langle r^2 \rangle$)].

| State | Nature | SAC-CI | | | Expt. |
|-----------|-----------------------------|-----------------|--------|-----------------------|---|
| | | ΔE (eV) | f | $\langle r^2 \rangle$ | |
| 1 1A_g | Ground state | | | 680.1 | |
| 1 1B_g | $\pi-\sigma^*$ | 6.25 | ... | 692.5 | 6.01 ^a |
| 1 1B_u | $\pi-\pi^*$ | 6.49 | 0.3440 | 681.9 | 6.35, ^b 6.36, ^c 6.58, ^d 6.26, ^e 6.28 ^f |
| 1 1A_u | $\pi-3s$ | 6.66 | 0.0000 | 709.4 | |
| 2 1B_g | $\pi-3p\sigma_y$ | 7.18 | ... | 724.8 | 7.44 ^g |
| 2 1A_u | $\pi-3d\sigma/\pi-\sigma^*$ | 7.44 | 0.0001 | 724.0 | |
| 2 1A_g | $\pi-3p\pi$ | 7.55 | ... | 743.8 | 7.40 ^g |
| 3 1B_g | $\pi-3p\sigma_x$ | 7.72 | ... | 750.8 | 7.51 ^g |
| 4 1B_g | $n^--\pi^*$ | 7.85 | ... | 676.9 | |
| 3 1A_u | $n^+-\pi^*/\pi-3d\sigma$ | 8.09 | 0.0038 | 721.7 | 8.13 ^g |
| 4 1A_u | $n^+-\pi^*/\pi-3d\sigma$ | 8.13 | 0.0009 | 728.2 | 8.13 ^g |
| 2 1B_u | $n^--\sigma^*$ | 8.22 | 0.0073 | 690.5 | |
| 3 1B_u | $\pi-3d\pi$ | 8.29 | 0.0351 | 803.1 | 8.11, ^c 8.14 ^g |
| 5 1A_u | $\pi-3d\sigma$ | 8.30 | 0.0003 | 816.0 | 8.21 ^g |
| 3 1A_g | $n^+-\sigma^*$ | 8.34 | ... | 690.6 | |
| 4 1B_u | $\pi-3d\pi$ | 8.41 | 0.0149 | 823.6 | 8.23 ^g |
| 5 1A_g | n^--3s | 8.89 | ... | 731.0 | |
| 5 1B_u | n^+-3s | 9.06 | 0.1048 | 725.3 | |

^aReference 22.

^bReference 17.

^cReference 2.

^dReference 14.

^eReference 8.

^fReference 4.

^gReference 19.

III. RESULTS AND DISCUSSIONS

The chlorine atom has two nonbonding orbitals n , one in plane and the other out of plane. However, the selected chloroethylenes have two or more chlorine atoms, and because of the interactions between the chlorine atoms, the nonbonding orbitals split into more orbitals. For example, in dichloroethylene, the n orbitals split into four orbitals and in tetrachloroethylene these split into eight. Pictorial representations of some of these orbitals involved in the excitations studied in the present study and other important σ^* antibonding orbitals and their notations (n^- , n^+ , n_\perp , σ_-^* , σ_+^* , and σ_0^*) used in the report are given in the EPAPS file.⁴⁶

A. *trans*-dichloroethylene

Electronic-state calculations for the *trans*-dichloroethylene were made within C_{2h} symmetry, with the molecule placed in the xy plane. Table I shows the vertical excitation energies and oscillator strengths obtained using the SAC-CI theory with the available experimental values.

As expected, there are many excited states within the 9 eV range. Unlike the situation with the fluoroethylene counterpart,³⁹ many transitions can be seen from the nonbonding chlorine n orbitals because the chlorine atom is less electronegative than the fluorine atom. The main excitation is the $\pi \rightarrow \pi^*$ transition at 6.49 eV with an oscillator strength of 0.34. An oscillator strength of around 0.4 is expected for chloroethylenes.¹⁴ The calculated $\pi \rightarrow \pi^*$ excitation energy agrees excellently with the experimental values. A peak at 6.01 eV was assumed to be due to the $\pi-\sigma^*$ state,²² and our results support that assumption. All other calculated values agree well with the available experimental values. A peak at

8.23 eV observed in an earlier experimental study was assumed to be due to either the Rydberg $\pi-3d\pi$ or $n-3s$ state.¹⁹ The present study supports the assignment of the former state. All of the Rydberg states were identified, including the $\pi-3s$ state, which has not been seen before in this chloroethylene. As mentioned in Sec. I, the calculations by Umemoto *et al.*²⁷ found that two $\pi-\sigma^*$ states and one $n-\sigma^*$ state are located below the main $\pi-\pi^*$ state and, accordingly, they proposed the dissociation mechanisms in the dichloroethylenes. In fact, a few other studies later also proposed the photodissociation mechanisms based on the calculated results of Umemoto *et al.*²⁷ However, the high-level calculations in the present study show a different scenario, in which only one $\pi-\sigma^*$ state exists below the bright $\pi-\pi^*$ state and, contrary to the earlier prediction,²⁷ the first $n-\sigma^*$ state was also calculated to be located above the main $\pi-\pi^*$ state. Thus, unlike previous conclusions, predissociation (CI detachment) from the excited $\pi-\pi^*$ state to the first $n-\sigma^*$ state is also possible. Hence, transition to both the dissociative $n-\sigma^*$ states from the initially excited $\pi-\pi^*$ state due to level crossing is likely, which can ultimately give CI fragments. Although the aim of the present study was not to propose a dissociation mechanism, the results obtained in this study indeed reveal that reliable excitation energies are important for understanding the photochemistry of the chloroethylenes. The study reveals clearly that the existing proposed photodissociation schemes should be revised.

B. *cis*-dichloroethylene

The *cis*-dichloroethylene has C_{2v} symmetry and the electronic-state calculations were performed within this sym-

TABLE II. Low-lying singlet excited states of *cis*-dichloroethylene obtained using SAC-CI at experimental geometry (Ref. 47) [excitation energies (ΔE), oscillator strengths (f), and second moments ($\langle r^2 \rangle$)].

| State | Nature | SAC-CI | | | Expt. |
|-----------|---------------------------------|-----------------|--------|-----------------------|---|
| | | ΔE (eV) | f | $\langle r^2 \rangle$ | |
| 1 1A_1 | Ground state | | | 521.1 | |
| 1 1B_1 | $\pi-\sigma_-^*$ | 6.45 | 0.0001 | 536.7 | |
| 2 1B_1 | $\pi-3s$ | 6.71 | 0.0028 | 566.6 | |
| 1 1B_2 | $\pi-\pi^*$ | 6.93 | 0.4176 | 528.0 | 6.60, ^b 6.53, ^c 6.52 ^d |
| 1 1A_2 | $\pi-\sigma_+^*/\pi-3p\sigma_y$ | 7.48 | ... | 570.8 | 7.33 ^{a,e} |
| 3 1B_1 | $\pi-3p\sigma_z$ | 7.61 | 0.0087 | 571.8 | 7.41 (or) 7.56 ^{a,e,f} |
| 2 1A_1 | $\pi-3p\pi$ | 7.67 | 0.0163 | 593.0 | 7.41 (or) 7.56 ^{a,e,f} |
| 2 1A_2 | $\pi-3p\sigma_y$ | 7.80 | ... | 595.3 | 7.33, ^{a,e} 7.35 ^f |
| 3 1A_2 | $n^+-\pi^*$ | 8.04 | ... | 525.6 | |
| 2 1B_2 | $n^--\sigma_-^*$ | 8.24 | 0.0098 | 536.4 | |
| 4 1B_1 | $\pi-3d\sigma$ | 8.32 | 0.0094 | 628.1 | 8.16 ^f |
| 5 1B_1 | $\pi-3d\sigma$ | 8.36 | 0.0051 | 646.6 | |
| 3 1A_1 | $n^+-\sigma_-^*$ | 8.38 | 0.0031 | 554.6 | |
| 3 1B_2 | $\pi-3d\pi$ | 8.42 | 0.0116 | 656.1 | 8.16 ^f |
| 4 1A_1 | $\pi-3d\pi/np\pi$ | 8.43 | 0.0004 | 622.3 | 8.16 ^f |
| 4 1A_2 | $\pi-3d\sigma$ | 8.73 | ... | 718.9 | |
| 4 1B_2 | n^--3s | 8.79 | 0.0701 | 571.8 | 8.16 ^f |
| 5 1A_1 | $n^+-3s/\pi-np\pi$ | 9.00 | 0.0002 | 611.1 | 8.22 ^f |

^aAdiabatic energy.

^bReference 17.

^cReferences 2 and 14.

^dReference 9.

^eReference 21.

^fReference 19.

metry with the molecule placed in the yz plane, where the y axis is the molecular axis. The calculated results were summarized in Table II with the available experimental values.

Table II reveals that the excitation energy calculated for the $\pi-\pi^*$ state has around 0.3 eV difference with that of the experimental value, but by considering that it is not easy to get excellent agreement between the theoretical and experimental values for the $\pi \rightarrow \pi^*$ transitions in the ethylenic molecules,^{20,35,39} the difference of about 0.3 eV obtained in the present study is acceptable. The oscillator strength derived for the main $\pi \rightarrow \pi^*$ transition in *cis*-dichloroethylene was larger than that in the *trans* counterpart because of the delocalization of the π and π^* molecular orbitals over the chlorine $3p\pi$ orbital. The calculated values for the other transitions agree well with the experimental values. One should remember that the experimental values for the $\pi \rightarrow 3p$ transitions seen in the table are adiabatic ones.²¹ Also, some of the transitions in the experimental study have overlapping features.¹⁹ A band found at 8.16 eV in earlier experimental studies was suggested to be either a $\pi-4s$ or a $\pi-3d$ state.^{9,48} Later, through resonance-enhanced multiphoton ionization spectroscopic studies, Williams and Cool¹⁹ revealed that this transition was contributed by a closely located triplet band origin rather than a single origin, as suggested by earlier studies. Polarization measurements showed that two of these are totally symmetric and the remaining one was nonsymmetric. Williams and Cool¹⁹ suggested that one of the symmetric peaks might be due to the $n \rightarrow 3s$ transition and the remaining two are due to one symmetric and one nonsymmetric $\pi \rightarrow 3d$ transitions. Although a similar kind of closely located transition was noticed, the present study seems not to support the assignment of the $n \rightarrow 3s$ transition, but the results obtained here agree well

with the other two assignments, $\pi \rightarrow 3d$. Again, unlike the findings of Umemoto *et al.*,²⁷ only one $\pi-\sigma^*$ state exists below the main $\pi-\pi^*$ state. As in the case of *trans*-dichloroethylene, both the $n-\sigma^*$ states are located above the $\pi-\pi^*$ state, which is again different from the earlier prediction.

C. Tetrachloroethylene

Tetrachloroethylene has D_{2h} symmetry. All of the calculations were done keeping this symmetry, with the molecule placed in the yz plane, where the z axis is the molecular axis. The calculated excitation energies along with the available experimental values were tabulated in Table III.

The main transition is the $\pi \rightarrow \pi^*$ excitation. The calculated value, 6.41 eV, for the $\pi-\pi^*$ state agrees well with the experimental values. A few tentative assignments were made in the experimental studies and for most of the cases, our results support those previous assignments. As mentioned earlier, the $\pi \rightarrow 3s$ transition in tetrachloroethylene was ill defined in earlier experimental studies; one report² concluded that a peak of this $\pi \rightarrow 3s$ Rydberg transition is around 6.2 eV and another²¹ suggested that it should be around 6.58 eV. The present study supports the latter assignment. The existence of a valence transition at 7.68 eV in the experimental spectrum^{2,7} was tentatively assigned due to the $n_{\perp} \rightarrow \pi^*$ transition.¹⁵ The results obtained in the present study seem, however, not to support that assignment. On the other hand, the study supports the earlier assignment for the $n-\sigma^*$ state at 7.67 eV.²² As it is seen in both dichloroethylenes, at least one of the $n-\pi^*$ states is located below the dissociative $n-\sigma^*$ state. It is interesting to note that, unlike in the dichloroethylenes, all of the $\pi-\sigma^*$ states were located below the main $\pi-\pi^*$

TABLE III. Low-lying singlet excited states of tetrachloroethylene obtained using SAC-CI at experimental geometry (Ref. 49) [excitation energies (ΔE), oscillator strengths (f), and second moments ($\langle r^2 \rangle$)].

| State | Nature | SAC-CI | | | Expt. |
|--------------|------------------|-----------------|--------|-----------------------|---|
| | | ΔE (eV) | f | $\langle r^2 \rangle$ | |
| 1 1A_g | Ground state | | | 1285.1 | |
| 1 $^1B_{1g}$ | $\pi-\sigma_+^*$ | 5.76 | ... | 1291.1 | 5.39 ^b |
| 1 $^1B_{3u}$ | $\pi-\sigma_0^*$ | 6.30 | 0.0004 | 1299.5 | |
| 1 $^1B_{2g}$ | $\pi-\sigma_-^*$ | 6.33 | ... | 1296.7 | |
| 1 $^1B_{1u}$ | $\pi-\pi^*$ | 6.41 | 0.4973 | 1284.8 | 6.21, ^c 6.30, ^d 6.20, ^e 6.24, ^f 6.25 ^g |
| 2 $^1B_{3u}$ | $\pi-3s$ | 6.72 | 0.0171 | 1312.4 | 6.25, ^h 6.58 ^{a,d} |
| 2 $^1B_{1g}$ | $n^--\pi^*$ | 7.28 | ... | 1280.9 | |
| 2 1A_g | $\pi-3p\pi$ | 7.50 | ... | 1356.7 | 7.21 ⁱ |
| 3 $^1B_{1g}$ | $\pi-3p\sigma_y$ | 7.65 | ... | 1385.6 | 7.24 ⁱ |
| 2 $^1B_{2g}$ | $\pi-3p\sigma_z$ | 7.66 | ... | 1384.3 | 7.32 ⁱ |
| 1 $^1B_{3g}$ | $n^--\sigma_0^*$ | 7.91 | ... | 1292.7 | |
| 1 $^1B_{2u}$ | $n^--\sigma_-^*$ | 7.94 | 0.0092 | 1292.1 | 7.67, ^b 7.68 ^j |
| 3 $^1B_{3u}$ | $\pi-3d\sigma$ | 7.99 | 0.0025 | 1404.3 | |
| 1 1A_u | $\pi-3d\sigma$ | 8.02 | ... | 1411.1 | |
| 2 $^1B_{1u}$ | $n^--\sigma_+^*$ | 8.08 | 0.0018 | 1295.0 | |
| 2 $^1B_{2u}$ | $\pi-3d\pi$ | 8.13 | 0.0171 | 1423.7 | |
| 3 $^1B_{1u}$ | $\pi-3d\pi$ | 8.17 | 0.0002 | 1432.1 | |
| 4 $^1B_{3u}$ | $\pi-3d\sigma$ | 8.21 | 0.0005 | 1450.2 | |
| 3 $^1B_{2u}$ | $n_\perp-\pi^*$ | 8.44 | 0.1785 | 1283.5 | |
| 3 $^1B_{3g}$ | n^--3s | 8.68 | ... | 1321.4 | |
| 5 1A_g | $n^+-\sigma_+^*$ | 9.14 | ... | 1296.6 | |

^aAdiabatic energy.

^bReference 22.

^cReference 17.

^dReference 21.

^eReferences 14 and 15.

^fReferences 2 and 7.

^gReference 5.

^hReference 16.

ⁱReference 18.

^jReference 15.

state. Thus, the photodissociation mechanism in tetrachloroethylene is expected to be different from that in the dichloroethylenes. One of the $n \rightarrow \pi^*$ transitions, $n_\perp \rightarrow \pi^*$, is seen to have a large oscillator strength, so it is expected that this $n-\pi^*$ state has a significant role in the photodissociation of tetrachloroethylene at lower wavelength regions.

The triplet excitation energies calculated for *trans*- and *cis*-dichloroethylenes and tetrachloroethylene are tabulated in Table IV. In all the three chloroethylene cases, the experimental values are available only for the $\pi \rightarrow \pi^*$ triplet excitation. As the table shows clearly, the calculated triplet $\pi-\pi^*$ excitation energies agree very well with their experimental values.

D. Chlorofluoroethylenes

We have studied the electronic spectra of various chloro- and fluoroethylenes, and it would be interesting to examine the chlorofluoroethylenes, which would give us an opportunity to investigate the effects of two different substituent halogen atoms on the electronic states of ethylene. Therefore, in the present investigation we studied the electronic spectra of two such chlorofluoroethylenes: *trans*-1-chloro-2-fluoroethylene and *cis*-1-chloro-2-fluoroethylene. The singlet excitation energies with oscillator strengths obtained for these two chlorofluoroethylenes using SAC-CI calculations are tabulated in Tables V and VI along with the available experimental values.

Table V shows the results derived for *trans*-1-chloro-2-fluoroethylene. It should be noted that all of the n orbitals mentioned here belong to the Cl nonbonding orbitals and the σ^* orbitals are like those in dichloroethylenes, but the C-Cl bond domination is high. The main excitation once again is the $\pi \rightarrow \pi^*$ transition. The value calculated for this bright $\pi-\pi^*$ state, 6.94 eV, agrees excellently with the experimental value of 6.9 eV. This good agreement between the calculated and the experimental values also continues in the remaining states. In the experimental study,⁵¹ the $\pi \rightarrow 3s$ transition is estimated to be near 6.9 eV by extrapolating the experimental data and it was assumed that this $\pi-3s$ state is buried under the broad $\pi \rightarrow \pi^*$ band. The present study strongly supports those conclusions.

The results obtained for *cis*-1-chloro-2-fluoroethylene are summarized in Table VI. As in the case of *trans*-chlorofluoroethylene, all of the calculated values agree well with the experimental values. Once again, the extrapolated value for the $\pi \rightarrow 3s$ transition is supported by the calculated value.

E. The $\pi \rightarrow \pi^*$ transition

The main excitation in all of the studied haloethylenes was the $\pi \rightarrow \pi^*$ excitation. Analysis of the results derived for this main transition in the haloethylenes would reveal some interesting facts. The calculated $\pi-\pi^*$ excitation energies for the dihalogenated ethylenes and for ethylene are summarized in Table VII. All of the values presented in this table were

TABLE IV. Low-lying triplet excited states of *trans*- and *cis*-dichloroethylenes and tetrachloroethylene obtained using SAC-CI at their respective experimental geometries. Excitation energies (ΔE) are in eV (values in the parentheses are the experimental values taken from Ref. 17).

| <i>trans</i> -dichloroethylene ^a | | | <i>cis</i> -dichloroethylene ^a | | | Tetrachloroethylene ^b | | |
|---|------------------|----------------|---|-------------------|----------------|----------------------------------|------------------|----------------|
| State | Nature | ΔE | State | Nature | ΔE | State | Nature | ΔE |
| 1 3B_u | $\pi-\pi^*$ | 3.97 (3.84) | 1 3B_2 | $\pi-\pi^*$ | 4.00 (3.94) | 1 $^3B_{1u}$ | $\pi-\pi^*$ | 3.53 (3.54) |
| 1 3B_g | $\pi-\sigma_-^*$ | 6.00 | 1 3B_1 | $\pi-\sigma_-^*$ | 6.07 | 1 $^3B_{1g}$ | $\pi-\sigma_+^*$ | 5.31 |
| 1 3A_u | $\pi-3s$ | 6.64 | 2 3B_1 | $\pi-3s$ | 6.65 | 1 $^3B_{2g}$ | $\pi-\sigma_-^*$ | 5.92 |
| 2 3B_g | $\pi-3p\sigma_y$ | 7.19 | 1 3A_2 | $\pi-\sigma_+^*$ | 7.14 | 1 $^3B_{3u}$ | $\pi-\sigma_0^*$ | 6.04 |
| 2 3A_u | $\pi-3d\sigma$ | 7.29 | 2 3B_2 | $n^--\sigma_-^*$ | 7.52 | 2 $^3B_{3u}$ | $\pi-3s$ | 6.67 |
| 1 3A_g | $\pi-3p\pi$ | 7.53 | 3 3B_1 | $\pi-3p\sigma_z$ | 7.53 | 1 $^3B_{3g}$ | $n^--\sigma_0^*$ | 7.22 |
| 3 3B_g | $\pi-3p\sigma_x$ | 7.70 | 1 3A_1 | $\pi-3p\pi$ | 7.61 | 1 $^3B_{2u}$ | $n^--\sigma_-^*$ | 7.48 |
| 2 3B_u | $n^--\sigma_-^*$ | 7.72 | 2 3A_2 | $\pi-3p\sigma_y$ | 7.68 | 1 3A_g | $\pi-3p\pi$ | 7.48 |
| 2 3A_g | $n^+-\sigma_-^*$ | 7.80 | 2 3A_1 | $n^+-\sigma_-^*$ | 7.69 | 2 $^3B_{1u}$ | $n^--\sigma_+^*$ | 7.57 |
| 3 3A_u | $\pi-3d\sigma$ | 8.08 | 3 3A_1 | $\pi-3d\pi/np\pi$ | 8.38 | 2 $^3B_{1g}$ | $\pi-3p\sigma_y$ | 7.60 |
| 3 3B_u | $\pi-3d\pi$ | 8.25 | 3 3B_2 | $\pi-3d\pi$ | 8.41 | 2 $^3B_{2g}$ | $\pi-3p\sigma_z$ | 7.65 |
| | | | 3 3A_2 | $\pi-3d\sigma$ | 8.60 | 1 3A_u | $\pi-3d\sigma$ | 7.73 |
| | | | | | | 3 $^3B_{3u}$ | $\pi-3d\sigma$ | 7.98 |
| | | | | | | 2 $^3B_{2u}$ | $n_\perp-\pi^*$ | 8.13 |
| | | | | | | 3 $^3B_{2u}$ | $\pi-3d\pi$ | 8.16 |
| | | | | | | 3 $^3B_{1u}$ | $\pi-3d\pi$ | 8.17 |
| | | | | | | 2 $^3B_{3g}$ | n^--3s | 8.68 |

^aExperimental geometry from Ref. 47.

^bExperimental geometry from Ref. 49.

calculated at the same level of theory. There are two dominating effects due to the halogen substitution in the present case; one is the stabilizing inductive effect due to the electronegative halogen atoms and the other is the destabilizing resonance or repulsive effect due to the interaction between the vinyl group and the nonbonding orbitals of the halogen atoms. In the case of fluoroethylenes, because of the *perfluoro effect*,⁵² i.e., the selective stabilization of the σ orbitals and the insensitivity of the π orbitals, the $\pi \rightarrow \pi^*$ excitation energies are more or less the same as in ethylene.³⁹ That is, the stabilizing inductive effect is countered by the destabilizing repulsive effect in fluoroethylenes. In the case

of chlorinated ethylenes, however, the repulsive resonance interaction dominates the stabilizing inductive effect because of the small separation between the π orbital of the vinyl group and the nonbonding orbitals of chlorine atoms. This antibonding combination between these π and n orbitals destabilizes the π orbitals. For the unoccupied π^* orbitals, the resonance interaction should be less important because of the high-energy difference between the interacting orbitals. That means that the inductive effect dominates on π^* orbitals. For these reasons, the $\pi-\pi^*$ excitation energy in chloroethylenes must be smaller than that in ethylene. The $\pi-\pi^*$ excitation energies in the chlorofluoroethylenes should be in between

TABLE V. Low-lying singlet excited states of *trans*-1-chloro-2-fluoroethylene obtained using SAC-CI at experimental geometry (Ref. 50) [excitation energies (ΔE), oscillator strengths (f), and second moments ($\langle r^2 \rangle$) (n orbital belongs to Cl atom)].

| State | Nature | SAC-CI | | | Expt. ^a |
|-----------|------------------|-----------------|--------|-----------------------|--------------------|
| | | ΔE (eV) | f | $\langle r^2 \rangle$ | |
| 1 $^1A'$ | Ground state | | | 443.5 | |
| 1 $^1A''$ | $\pi-\sigma_-^*$ | 6.41 | 0.0048 | 456.9 | |
| 2 $^1A''$ | $\pi-3s$ | 6.90 | 0.0015 | 483.7 | 6.9 |
| 2 $^1A'$ | $\pi-\pi^*$ | 6.94 | 0.2899 | 451.3 | 6.9 |
| 3 $^1A''$ | $\pi-3p\sigma_y$ | 7.28 | 0.0000 | 491.0 | |
| 3 $^1A'$ | $\pi-3p\pi$ | 7.67 | 0.0034 | 508.9 | 7.58 |
| 4 $^1A''$ | $\pi-3p\sigma_x$ | 7.85 | 0.0117 | 501.3 | |
| 5 $^1A''$ | $\pi-3d\sigma$ | 8.20 | 0.0016 | 531.4 | |
| 4 $^1A'$ | $n-\sigma_-^*$ | 8.37 | 0.0010 | 454.4 | 8.5 |
| 6 $^1A''$ | $\pi-3d\sigma$ | 8.38 | 0.0061 | 568.8 | |
| 7 $^1A''$ | $\pi-3d\sigma$ | 8.42 | 0.0023 | 572.8 | |
| 5 $^1A'$ | $\pi-3d\pi$ | 8.47 | 0.0082 | 586.2 | |
| 6 $^1A'$ | $\pi-3d\pi$ | 8.56 | 0.0363 | 586.6 | |

^aReference 51.

TABLE VI. Low-lying singlet excited states of *cis*-1-chloro-2-fluoroethylene obtained using SAC-CI at experimental geometry (Ref. 50) [excitation energies (ΔE), oscillator strengths (f), and second moments ($\langle r^2 \rangle$) (n orbital belongs to Cl atom)].

| State | Nature | SAC-CI | | | Expt. ^a |
|-----------|-------------------|-----------------|--------|-----------------------|--------------------|
| | | ΔE (eV) | f | $\langle r^2 \rangle$ | |
| 1 $^1A'$ | Ground state | | | 368.0 | |
| 1 $^1A''$ | $\pi-3s/\sigma^*$ | 6.47 | 0.0069 | 389.2 | |
| 2 $^1A''$ | $\pi-3s$ | 6.79 | 0.0058 | 402.1 | 6.9 |
| 2 $^1A'$ | $\pi-\pi^*$ | 7.31 | 0.3762 | 381.7 | 7.11 |
| 3 $^1A''$ | $\pi-3p\sigma_y$ | 7.54 | 0.0044 | 427.7 | 7.59 |
| 3 $^1A'$ | $\pi-3p\pi$ | 7.70 | 0.0349 | 430.8 | 7.81 |
| 4 $^1A''$ | $\pi-3p\sigma_z$ | 7.80 | 0.0014 | 433.2 | |
| 4 $^1A'$ | $n-\sigma^*$ | 8.23 | 0.0056 | 380.5 | 8.5 |
| 5 $^1A''$ | $\pi-3d\sigma$ | 8.25 | 0.0020 | 458.6 | |
| 6 $^1A''$ | $\pi-3d\sigma$ | 8.40 | 0.0167 | 478.4 | |
| 7 $^1A''$ | $\pi-3d\sigma$ | 8.46 | 0.0014 | 500.6 | |
| 5 $^1A'$ | $\pi-3d\pi$ | 8.47 | 0.0005 | 496.5 | |
| 6 $^1A'$ | $\pi-3d\pi$ | 8.53 | 0.0319 | 500.1 | |

^aReference 51.

those in fluoro- and chloroethylenes. Our results support all of these facts clearly. One can notice from Table VII that the chloroethylenes' effect slightly dominates the fluoroethylenes' effect in the chlorofluoroethylenes. As Table VII indicates, in all three combinations, the $\pi-\pi^*$ excitation energies obtained for the *cis* conformers are higher than for their *trans* counterparts. This is due to the fact that, in the case of a *cis* conformer, both halogen atoms are on the same side, enhancing the antibonding character of π^* , resulting in higher excitation energies.

IV. CONCLUDING REMARKS

The electronic spectra of *trans*- and *cis*-dichloroethylenes and tetrachloroethylene, as well as chlorofluoroethylenes, were studied by using the SAC-CI theory with the aug-cc-pVTZ basis set of Dunning, Jr., incorporated with the necessary Rydberg *spd* functions.

The excitation energies calculated for the vertical as well as for the Rydberg states agree very well with the available experimental values in all cases, including for the difficult $\pi-\pi^*$ states. The calculated oscillator strengths clearly reveal that the $\pi-\pi^*$ state is the optically bright state in all of the studied chloroethylenes. Through the present study, we can identify and assign $\pi \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, and $n \rightarrow \pi^*$ vertical transitions that have not been studied before. Some of these

states are expected to be involved in the photodissociation of these chloroethylenes. Various speculative assignments made through earlier experimental studies were clarified. Many Rydberg states, including the $\pi-3s$ state, which were not clearly seen before were also studied. Vertical excitations in two chlorofluoroethylenes were also studied.

Unlike in the earlier studies, all of the dissociative $n-\sigma^*$ states in the studied chloroethylenes were calculated to be located above the optically bright $\pi-\pi^*$ state. Hence, contrary to the earlier conclusions, the predissociation from the bright $\pi-\pi^*$ state to all of these $n-\sigma^*$ states was highly possible. In the case of $\pi-\sigma^*$ states, the present study also reveals a different scenario about their locations from that seen in the earlier study. Consequently, the present accurate *ab initio* study clearly indicates that the photodissociation mechanisms in the dichloroethylenes proposed using the earlier calculations warrant a revision.

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TABLE VII. $\pi-\pi^*$ excitation energies (ΔE) of dihaloethylenes.

| Molecule | ΔE (eV) |
|---|-------------------|
| Ethylene | 7.96 ^a |
| <i>trans</i> -difluoroethylene | 7.79 ^b |
| <i>cis</i> -difluoroethylene | 8.12 ^b |
| <i>trans</i> -dichloroethylene | 6.49 |
| <i>cis</i> -dichloroethylene | 6.93 |
| <i>trans</i> -1-chloro-2-fluoroethylene | 6.94 |
| <i>cis</i> -1-chloro-2-fluoroethylene | 7.31 |

^aValues were taken from our earlier reports, Ref. 35.

^bValues were taken from our earlier reports, Ref. 39.

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